Conformational Analysis of [60]PCBM via 2nd-Order Proton NMR Spin-Spin Coupling Effects

Journal:	*The Journal of Physical Chemistry Letters*
Manuscript ID	jz-2020-01421b.R3
Manuscript Type:	Letter
Date Submitted by the Author:	17-Jun-2020
Complete List of Authors:	Liu, Tong; Queen Mary University of London, School of Physics and Astronomy Abrahams, Isaac; Queen Mary University of London, School of Biological and Chemical Sciences Dennis, Terence; Queen Mary University of London, School of Physics and Astronomy

Conformational Analysis of [60]PCBM via 2nd-Order Proton NMR Spin-Spin Coupling Effects

*Tong Liu,[1] I. Abrahams,[2] T. John S. Dennis[1]**

1 School of Physics and Astronomy, Queen Mary University of London, Mile End Road, London, E1 4NS, UK.

2 School of Biological and Chemical Sciences, Queen Mary University of London, Mile End Road, London, E1 4NS, UK.

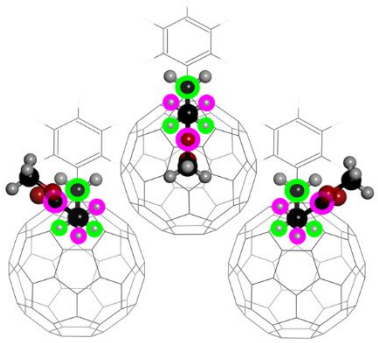
AUTHOR INFORMATION

Corresponding Author

* T. J. S. Dennis. Email j.dennis@qmul.ac.uk

The ^{1}H NMR spectrum of [60]PCBM was recorded at high resolution (600 MHz). All ^{1}H resonances expected of the C_s symmetry molecule were observed. The spin-spin couplings in the ^{1}H NMR spectrum were not as expected at 1st order. Instead, the effects of AA′BB′-type 2nd-order couplings are clearly observed for the protons attached to both ester carbons C3 and C4, which were analyzed in terms of 7 coupling constants. This indicates that there is no free rotation of the sigma bonds of the alkyl chain in the ester group – although rotation becomes free at a larger distance from the fullerene bridge carbon (C61). The ^{1}H results further indicated that there is a 1:6:1 population ratio of the three staggered conformers (*gauche-anti-gauche*′) about the ester group C3-C4 bond. These results may aid in the understanding of the morphological interactions between [60]PCBM and its surroundings in condensed-phase organic electronic devices such as organic and perovskite photovoltaics.

TOC GRAPHICS



KEYWORDS PCBM, structure, geometry, multiplet, coupling constant, staggered conformer.

Phenyl butyric acid methyl ester ([60]PCBM), or more properly in IUPAC nomenclature, methyl 4-[61-phenyl,3a*H'* -cyclopropa-1,9-(C_{60}-I_h)[5,6]-fullerenyl]butanote, is one of the most important molecules in organic electronics; serving as an n-type material in bulk heterojunction and perovskite photovoltaics, field effect transistors, light emitting diodes and photodetectors.[1-7] It was first reported by Hummelen et al. in 1995 as one of several methano-bridged fullerene derivatives they had newly synthesized (and termed M1OMe at the time).[8] Amongst other things, they reported the ^{1}H nuclear magnetic resonance (NMR) spectral line positions of [60]PCBM. This included describing the resonances related to the C_3H_6 alkyl chain as being "multiplets," This behavior is unexpected, as the ^{1}H NMR spectrum of this part of the molecule should show spin-spin couplings that give rise to a series of three 1:2:1 Pascal triangle triplets from the splitting by CH_2 groups. However, although reported, this was not commented on, or analyzed. In addition, two subsequent reports of the ^{1}H NMR spectrum[9,10] did not mention this multiplet behavior.

In this paper we analyze the spin-spin coupling structure of these previously identified ^{1}H multiplets in terms of AA'BB'-type 2nd-order couplings that result from the hydrogens attached to carbons C2, C3 and C4 of the ester group. The 2nd-order effects occur because the two hydrogens attached to each of these carbons are symmetrically equivalent, but magnetically inequivalent. This behavior indicates there is restricted rotation about the bond between these two carbons. This analysis also gives insight into the relative populations at room temperature of the three staggered conformers (*gauche*, *anti* and *gauche*') about the C3-C4 bond of the ester group. To aid in the interpretation of the spectrum, Figure 1 depicts [60]PCBM with the hydrogens number in

accordance with the IUPAC label for the carbon they are attached to (e.g., H_4 and $H_{4'}$ are attached to ester carbon C4).

.

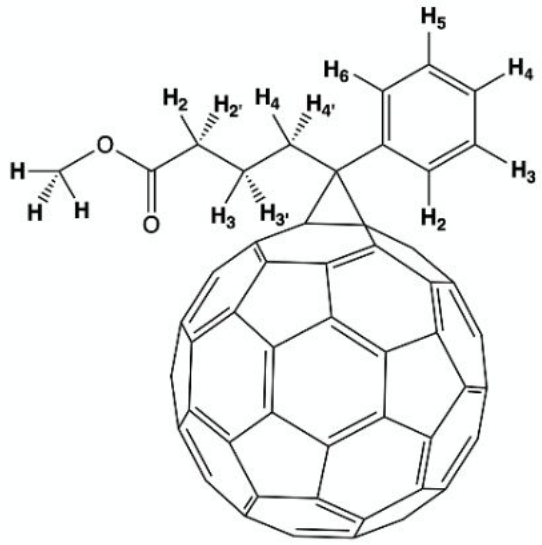


Figure 1. A diagram of [60]PCBM showing the hydrogen numbering system used in this letter.

Figure 2 shows the ^{1}H NMR spectrum of [60]PCBM. The insets show enlargements of individual resonances that indicate spin-spin couplings with matched intensities. In addition to the signals from [60]PCBM, the full spectrum exhibits several other resonances from contaminants. Primary among these are resonances from toluene are a singlet at 2.26 ppm from the methyl group; a triplet at 7.09 ppm from the hydrogens attached to the toluene carbon C4, and the coincidence of a doublet (from the 7.20 ppm.

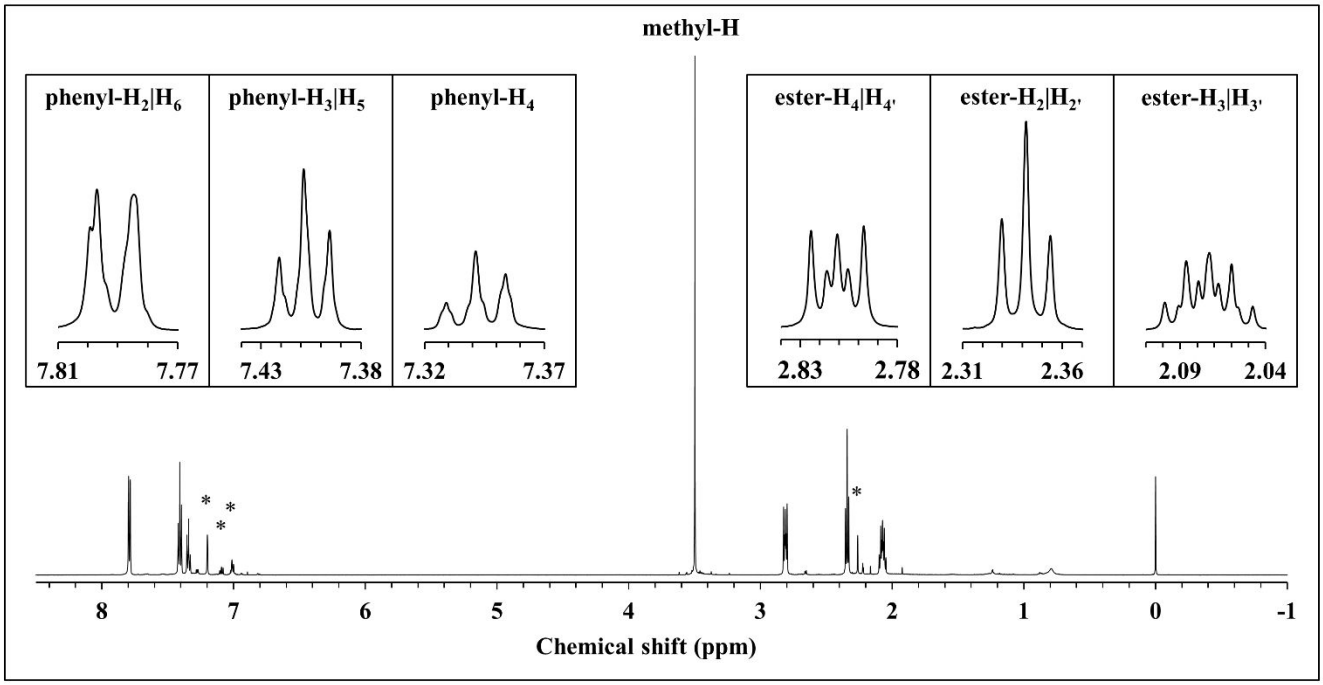


Figure 2. The ^{1}H NMR spectrum of [60]PCBM recorded in CS_2 solution at 300 K. The insets show the spin-spin splitting of resonances from the phenyl ring and the C_3H_6 part of the ester group. The asterisks denote resonances from toluene and benzene from the sample preparation which were tenaciously retained, and the singlet at 0.00 ppm is the TMS reference.

That the resonances shown in Figure 2 are from [60]PCBM is confirmed by three main indicators. Firstly, they occur at the expected chemical shifts for [60]PCBM; secondly, their integrations are all consistent with those expected of [60]PCBM – with all in near-integer ratios (to two significant figures); and finally, they are consistent with the previous report from the original synthesis.[8]

Discussing the aliphatic protons first, the singlet at 3.50 ppm, of integration 3H, is clearly from the three methyl protons. The remaining three resonances at 2.81, 2.34 and 2.07 ppm, all of integration 2H, are from the -CH2-CH2-CH2- chain. These show as a 5-peak multiplet, a 1:2:1 triplet and a 9-peak multiplet, respectively.

Based on typical group resonance values the 1H resonance with the lowest chemical shift (2.07 ppm) may be assigned to hydrogens attached to the central carbon of this chain (carbon C3 of the methyl butanoate group) and the resonance with the highest chemical shift (2.81 ppm) assigned to the hydrogens attached to the C4 carbon of that group. This leaves the resonance at 2.34 ppm as originating from the hydrogens of C2. These assignments concur with those from Ref. 1.

At first order, the resonance from the two chemically equivalent hydrogens attached to carbon C4 of the methyl butanoate group is expected to show spin-spin coupling to the two chemically equivalent hydrogens attached to the neighboring carbon C3. As such, it should comprise a 1:2:1 triplet of integration $I = 2$, with a spin-spin coupling constant ${}^3J \sim 8$ Hz. However, what is observed for the C4 hydrogens is, at first sight, roughly a 2:1:2:1:2 pentet. This feature was previously reported as a 'multiplet' but not analyzed or explained.[8] Such a line pattern indicates that the two hydrogens of C4 are not magnetically equivalent to each other despite being symmetrically equivalent. Similarly, the two C3 hydrogens are also magnetically inequivalent. Hence, this system shows 2nd-order spin-spin couplings between the hydrogens of C4 and C3. The situation presented for the C4 hydrogens is a 4-spin AA′BB′ -type system; where A and A′ represent the two chemically equivalent, but magnetically

inequivalent, hydrogens attached to C4, and B and B′ represent their analogues attached to the neighboring carbon C3. This situation generally yields 4 coupling constants: $^3J_{AB}$, $^3J_{AB'}$, $^2J_{AA'}$ and $^2J_{BB'}$. Generally, the AA′BB′ system yields a spectrum that is comprised of 10 lines for the hydrogens at C4, resulting from a doublet, and two separate AB-type quartets. However, the measured spectrum contains 7 lines (close inspection of the abovementioned 5-line multiplet, reveals two very weak outer lines). Such a pattern is explained in Reference 11 and presented in Table 31 of that reference. It represents the situation where $^2J_{AA'}$ and $^2J_{BB'}$ are equal to within experimental error, which leads to coincidences of 3 lines. As such, the spectrum may be analyzed in terms of three features. The first is an intense doublet (2.79 and 2.83 ppm), centered on ν_A and has a separation of ($^3J_{AB} + {}^3J_{AB'}$). The second generally is an AB-type quartet – again centered on ν_A. However, with $^2J_{AA'} = {}^2J_{BB'}$, the two outer lines are coincidental in our case. This has the appearance of a doublet (2.80 and 2.82 ppm) of total separation of ($^3J_{AB} - {}^3J_{AB'}$). The third is another AB-type quartet centered on ν_A; which this time has the two central lines being coincidental. This yields a triplet (2.76, 2.81 and 2.86 ppm) with two equal separations of ($^2J_{AA'} + {}^2J_{BB'}$); this time the inner line is much more intense than the outer lines. Applying these analyses to the present spectrum indicates that: ν_A = 1683.82 Hz, on the instrument used, corresponding to a chemical shift of δ = 2.81 ppm from TMS. The splitting of the intense doublet indicated that $^3J_{AB} + {}^3J_{AB'} = {}^3J_{4,3} + {}^3J_{4,3'}$ = 16.4 Hz. The width of the 1st quartet indicates that $^3J_{AB} - {}^3J_{AB'} = {}^3J_{4,3} - {}^3J_{4,3'}$ = 6.8 Hz. From these it can be established that $^3J_{4,3}$ and $^3J_{4,3'}$ are 11.6 Hz and 4.8 Hz, respectively (as $^3J_{4,3} - {}^3J_{4,3'}$ is

positive, $^3J_{4,3} > {}^3J_{4,3'}$). Since $^2J_{AA'} = {}^2J_{BB}$, from the shape and spacings of the 2nd quartet, ($^2J_{AA'} + {}^2J_{BB'}$) = 27.5 Hz, in this case, it is established that $^2J_{4,4'} = {}^2J_{3,3'}$ = 13.8 Hz.

To test these analyses, this multiplet was simulated using the WinDNMR computer program[12] for an AA′BB′ system using the couplings established above, together with the experimental ν_A-ν_B difference of 430 Hz and the instrumental resolution (0.07 Hz). The result, shown in Figure 3, is remarkably like the experimental spectrum of this multiplet. The splittings and relative intensities, including the 2nd-order unevenness of those intensities of the simulation is effectively indistinguishable from experiment. This suggests that all the couplings for the protons on ester carbon C4 established from the 2nd-order analysis are reliable.

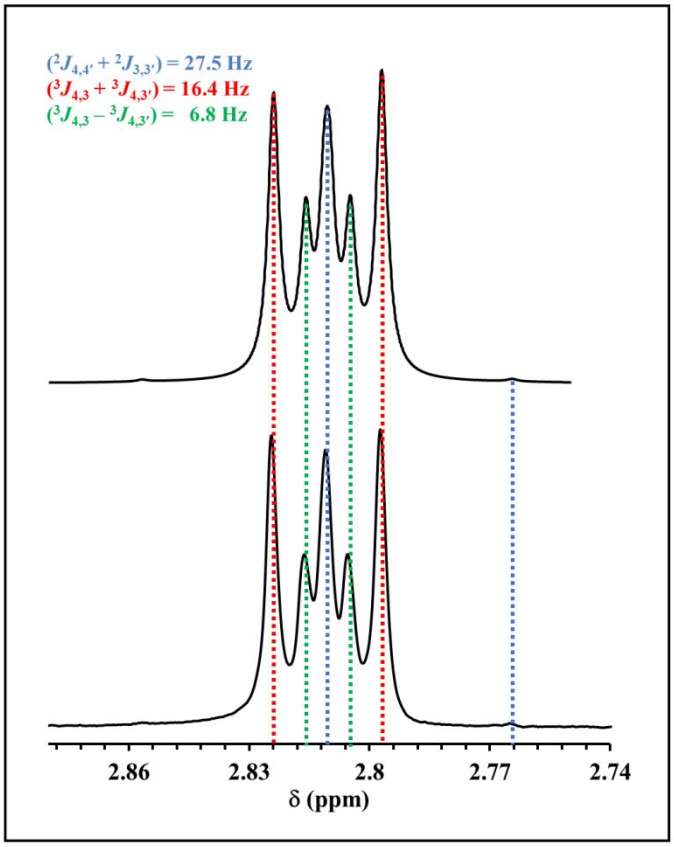


Figure 3. WinDNMR simulation (top) of the experimental spectrum (bottom) of the ester C4 protons based on an AA′BB′ system with $^{3}J_{4,3}$, $^{3}J_{4,3'}$ and $^{2}J_{4,4'}$ being 11.6, 4.8 and 13.8 Hz, respectively (from the shown experimental splittings), and on $\nu_4 - \nu_3$ being the experimental 430 Hz.

Staggered conformers are considerably more stable than eclipsed conformers. Hence, they are more likely to be populated. In addition, the presence of 2nd-order couplings between the hydrogens of the ester carbon C4 with those at C3 strongly suggests that there is an unevenly population amongst the three staggered conformers (*gauche*, *anti* and *gauche*′). This is because, even at 2nd-order, an equal population of all three conformers yields the normal 1st-order 1:2:1 triplet. This means that there is a preferred conformer resulting from hinderance to full rotation about the C3–C4 bond of the ester group. There is not usually any hindered rotation, and thereby no 2nd-order effects in the proton spectra of alkyl chains. As such, the hindered rotation about the ester C3–C4 bond, which gives rise to the 2nd-order effects, is most likely to originate from the thing that makes the difference – close proximity via direct bonding of C4 to the relatively huge phenyl-cyclopropafullerenyl group.

A reasonable estimate of the relative populations of the three staggered conformers may be obtained via the computer program MestReJ[13] using a Colucci-Jungk-Gandour analysis.[14] Although this program has empirical data for an ester substituent, it has none for a phenyl cyclopropafullerenyl group. However, making the reasonable substitution of phenyl group gives $^{3}J_{AB}$ = 3.36 Hz for the *anti* and *gauche* conformers and $^{3}J_{AB}$ = 14.37 Hz for the *gauche′*

conformer, and $^3J_{AB'}$ = 14.37 Hz for the *anti* conformer and $^3J_{AB}$ = 3.36 Hz for the *gauche* and *gauche'* conformers.

A population analysis based on these figures suggests the '*anti*' conformer is occupied for about 75% of the time, while the occupation times of the two *gauche* conformers are equal at about 12.5% each. This is because a 75:12.5:12.5 ratio gives $^3J_{4,3}$ = (0.75 × 14.37 + 0.125 × 3.36 + 0.125 × 3.36) = 11.6 Hz and also gives $^3J_{4,3'}$ = (0.75 × 3.36 + 0.125 × 3.36 + 0.125 × 14.37) = 4.8 Hz. This shows that it is only the population difference that is the cause of the 2nd-order effects. This is because if the populations are equal (one third each) then $^3J_{4,3}$ and $^3J_{4,3'}$ would be indistinguishable – giving only the 1st-order splitting. Indeed, substituting equal populations into the above equations yields a 1:2:1 triplet with $^3J_{4,3'}$ = $^3J_{4,3}$ = 7.1 Hz, which is typical of an alkyl chain.

The values of $^3J_{4,3}$ and $^3J_{4,3'}$ obtained via this analysis are both consistent with the experimental values of 11.6 and 4.8 Hz. It suggests that there is a strong preference for the '*anti*' conformer; whereby, the carbon C4 of the ester group lies along the mirror plane. However, there is some probability of rotation about the C3-C4 bond through the eclipsed conformer to the *gauche* staggered conformers on either side – but there is a negligible probability of rotation from the *gauche* conformer, through the conformer with the phenyl group and the remainder of the ester being eclipsed, to the *gauche'* staggered conformer. That is, through restricted rotation about the C3-C4 bond the ester group dynamically flips

back and forth between the two *gauche* conformers but only via the *anti* conformer; while spending most of its time in the middle (*anti* conformer).

The proton on carbon C2 of the ester group, at the other end of the -CH_2-CH_2-CH_2- chain, closely resembles a 1st-order 1:2:1 triplet with a chemical shift of δ = 2.34 ppm and a $^3J_{3,2}$ coupling, through protons on the middle carbon(C3), of 7.4 Hz. The presence of this triplet indicates that the populations of the three conformers of the type discussed above are effectively equally populated (i.e., that there is reasonably free rotation about the ester C2-C3 bond). Closer analysis indicated that there is also what appears to be a $^4J_{2,4}$ coupling to the hydrogens of ester carbon C4 with a coupling constant 1.7 Hz. Hence, this resonance appears as a triplet of triplets.

The resonance of the protons on the middle carbon (C3 of the ester group) has a chemical shift of δ = 2.07 ppm and is very complex – with some 10 components. Similarly to the protons of C4, this feature was previously reported as an unexplained multiplet.[8] However, as these protons are coupled to those on C4 (with its 2nd-order couplings) and to those on carbon C2 (with its 1st-order couplings), the coupling constants, of the protons on this carbon are those already determined ($^2J_{3,3'}$ = 13.8 Hz, $^3J_{3,4}$ = 11.6 Hz, $^3J_{3,4'}$ = 4.8 Hz, $^3J_{3,2}$ = 7.4 Hz).

Turning to the aromatic resonances, the three resonances at 7.79, 7.41, and 7.34 ppm (the insets on the left of Figure 2) are from the protons of the phenyl ring. The integration 2 line at 7.79 is clearly from the hydrogens attached to the symmetrically equivalent phenyl

carbons C2 and C6 (*ortho* position). This resonance seems to show the doublet of doublets pattern expected of this position. However, closer inspection reveals unresolved shoulders indicative of weak 2nd-order effects. This suggests that $^4J_{2,6}$ and $^4J_{3,5}$ are both vanishingly small. Although the additional 2nd-order peaks are seen, unlike for the C_3H_6 chain of the ester, the effect is so weak that no reliable measurement can be made of their resonance frequencies. Hence, the resonances from the phenyl C2|C6 hydrogens were analyzed in terms of their measurable 1st-order spin-spin splitting. That is, a ddd pattern with coupling constants $^3J_{2,3}$ = 7.8 Hz and $^4J_{2,4}$ = 1.3 Hz. The $^5J_{2,5}$ coupling constant although present was not resolved enough to be reliably determined from the spectrum.

The integration-2 resonance at 7.41 ppm is assigned to the phenyl hydrogens at C3/C5 (*meta* position). This resonance was reported as a 1:2:1 triplet.[8] However, it shows as a double doublet of doublets in which one line from each doublet is practically coincident – giving the effect of a triplet. This is evidenced by the fact the intense 'central' line is not at the center of the 'triplet'. Hence, two coupling constants were measured $^3J_{3,2}$ = 7.8 Hz and $^3J_{3,4}$ = 7.3 Hz. A doublet of doublets is expected for this resonance because the splitting of the C3 hydrogen by that at C2 is very close to but not identical to the splitting of the hydrogen as C3 by the one at C4. There is also evidence of further doublet splitting of this resonance by the hydrogen at phenyl C6 (as evidenced by shoulders) with $^5J_{3,6}$ = 2.0 Hz. As with the resonance for the hydrogens at C2/C6, there is evidence of immeasurable 2nd-order effects, as evidenced by weak unresolved shoulders on the lines. The ^{1}H integral resonance at 7.34 ppm

is assigned to the hydrogen at phenyl carbon C4 (*para* position) and shows as a triplet of triplets with coupling constants of $^{3}J_{4,3}$ = 7.3 Hz and $^{4}J_{4,2}$ = 1.3 Hz.

Table 1. The ^{1}H NMR chemical shifts, integrations, assignments and spin-spin coupling constants for [60]PCBM as extracted from the ^{1}H NMR spectrum. The multiplets both show strong 2nd-order spin-spin interactions from symmetrically equivalent but magnetically inequivalent protons.

Chemical shift/ppm	Int.	Assignment	Multiplet	Spin-spin coupling constant/Hz			
7.79	2H	*o*-Ph(C2/C6)	ddd	$^{3}J_{2,3}$ 7.8	$^{4}J_{2,4}$ 1.3	$^{5}J_{2,5}$ (unresolved)	
7.41	2H	*m*-Ph(C3/C5)	ddd	$^{3}J_{3,2}$ 7.8	$^{3}J_{3,4}$ 7.3	$^{5}J_{3,6}$ 2.0	
7.34	1H	*p*-Ph(C4)	tt	$^{3}J_{4,3}$ 7.3	$^{4}J_{4,2}$ 1.3		
3.50	3H	Me	s				
2.81	2H	Ph-C-**CH$_2$**-	2nd-order m	$^{2}J_{4,4'}$ 13.8	$^{3}J_{4,3}$ 11.6	$^{3}J_{4,3'}$ 4.8	
2.34	2H	-CH$_2$-**CH$_2$**-CO	tt	$^{3}J_{2,3}$ 7.4	$^{4}J_{2,4}$ 1.7		
2.07	2H	CH$_2$-**CH$_2$**-CH$_2$-	2nd-order m	$^{2}J_{3,3'}$ 13.8	$^{3}J_{3,4}$ 11.6	$^{3}J_{3,4'}$ 4.8	$^{3}J_{3,2}$ 7.4

In summary, spin-spin couplings in the 1H spectrum for the ester group in [60]PCBM were not as expected at 1st-order. Clear 2nd-order couplings are seen; revealing that the two protons on each of the three carbons of the C3H6 chain are not magnetically equivalent, despite being symmetrically equivalent. This indicates that there is restricted rotation about the sigma bond of the alkyl chain in ester group owing to steric effects from the bulky phenyl-cyclopropafullerenyl group. There is no full rotation about the ester bond connected directly to the fullerene bridge carbon (C61). However, the rotation becomes increasingly freer as the distance from the fullerene increases. This is evidenced by strong 2nd-order effects on the hydrogens at ester carbon C4, mixed effects at C3, and almost normal 1st order

free-rotation splitting at the hydrogens of ester carbon C2. Assuming an AA'BB'-type system, the hydrogens of ester carbons C3 and C4 revealed 7 coupling constants. It was also determined that there was hindered rotation about the ester C3–C4 bond, which yielded a 1:6:1 population ratio of the three staggered conformers (gauche-anti-gauche') about this bond. These hindered rotational and conformational conclusions may also provide insights into the packing behavior of [60]PCBM in the solid state;[15,16] and perhaps more importantly, it may aid in the understanding of the morphological interactions between [60]PCBM and its surroundings in condensed-phase organic electronic devices such as organic and perovskite photovoltaics.

[60]PCBM was synthesized via the method of Hummelen et al.[8] and purified following the method of Shi et al.[17] used to isolate the isomers of bis[60]PCBM. The ^{1}H NMR spectrum (16 co-added scans) was recorded at 300 K on Bruker AV600 spectrometer in CS_2 solution following the method of Liu et al.[18] for the ^{13}C NMR spectra of 19 purified isomers of bis[60]PCBM. Chemical shifts (ppm) are referenced to trimethylsilane (TMS) and reported to two decimal places with insignificant error, and the spin-spin couplings (Hz) are reported to 1 decimal point with an error of ±0.1 Hz. Step-by-step details of the synthesis, HPLC chromatogram and NMR experimental details given as Supporting Information.

ASSOCIATED CONTENT

Supporting Information.

The following files are available free of charge.

Synthesis, HPLC chromatogram and NMR experimental details (PDF)

AUTHOR INFORMATION

Notes

The authors declare no competing financial interests.

ACKNOWLEDGMENT

We thank the China Scholarship Council and Queen Mary University of London for a joint PhD studentship to Tong Liu; Dr Harold Toms of the School of Biological and Chemical Sciences at QMUL for assistance with recording the NMR spectrum. We also thank Mr Charles Gellet, a final-year undergraduate research project student within the School of Physics and Astronomy at QMUL, for his assistance in analyzing the 2nd-order aspects of the proton NMR spectrum.

REFERENCES

(1) Berger, P. R.; Kim, M. Polymer solar cells: P3HT:PCBM and beyond. *J. Renew. Sustain. Ener.* **2018**, *10*, 013508.

(2) Han, J.; Wang, H. -Y.; Wang, Y.; Yu, M.; Yuan, S.; Sun, P.; Qin, Y.; Guo, Z. -X.; Zhang, J. -P.; Ai, X. -C. Efficient promotion of charge separation and suppression of charge recombination by blending PCBM and its dimer as electron transport layer in inverted perovskite solar cells. *RSC Adv.* **2016**, *6*, 112512–12519.

(3) Cho, S.; Seo, J. H.; Lee, K.; Heeger, A. J. Enhanced Performance of Fullerene n-Channel Field-Effect Transistors with Titanium Sub-Oxide Injection Layer. *Adv. Funct. Mater.* **2009**, *19*, 1459–1464.

(4) Thompson, B. C.; Fréchet, J. M. J. Polymer–fullerene composite solar cells, *Angew. Chem., Int. Ed.* **2008**, *47*, 58–77.

(5) Liu, Z.; Parvez, K.; Li, R.; Dong, R.; Feng, X.; Müllen, K. Transparent Conductive Electrodes from Graphene/PEDOT:PSS Hybrid Inks for Ultrathin Organic Photodetectors. *Adv. Mater.* **2015**, *27*, 669–675.

(6) Zhao, X.; Liu, T.; Hou, X.; Liu, Z.; Shi, W.; Dennis T. J. S. [60]PCBM single crystals: remarkably enhanced band-like charge transport, broadband UV-visible-NIR photo-responsivity and improved long-term air-stability. *J. Mater. Chem. C* **2018**, *6*, 5489–5496.

(7) Szendrei, K.; Arema, K.; Jarzab, D.; Mikhnenko, O. V.; Gocalinska, A.; Saba, M.; Quochi, F.; Mura, A.; Bongiovanni, G.; Blom, P. W. M.; Heiss, W.; Loi, M. A. Solution-Processable Near-IR Photodetectors Based on Electron Transfer from PbS Nanocrystals to Fullerene Derivatives. *Adv. Mater.* **2009**, *21*, 683–687.

(8) Hummelen, J. C.; Knight, B. W.; LePeq, F.; Wudl, F.; Yao, J.; Wilkins, C. L. Preparation and Characterization of Fulleroid and Methanofullerene Derivatives. *J. Org. Chem.* **1995**, *60*, 532–538.

(9) Yang, C.; Hu, J. G.; Heeger, A. J. Molecular structure and dynamics at the interfaces within bulk heterojunction materials for solar cells. *J. Am. Chem. Soc.* **2006**, *128*, 12007–12013.

(10) Mens, R.; Chambon, S.; Bertho, S.; Reggers, G.; Ruttens, B.; D'Haen, J.; Manca, J.; Carleer, R.; Vanderzande, D.; Adriaensens, P. Description of the nanostructured

morphology of [6,6]-phenyl-C_{61}-butyric acid methyl ester (PCBM) by XRD, DSC and solid-state NMR. *Magn. Reson. Chem.* **2011**, *49*, 242–247.

(11) Garbisch, E. W. Analysis of Complex NMR Spectra for the Organic Chemist. *J. Chem. Edu.* **1968**, *45*, 480–493.

(12) Reich, H. J. WinDNMR: Dynamic NMR spectra for windows. *J. Chem. Edu.* **1995**, *72*, 1086.

(13) Navarro-Vazquez, A.; Cobas, J. C.; Sardina, F. J. A Graphical Tool for the Prediction of vaccinal proton-proton $^3J_{HH}$ coupling constants. *J. Chem. Inf. Comput. Sci.* **2004**, *44*, 1680–1685.

(14) Colucci, W. J.; Jungk, S. J; Gandour, R. D. An equation utilizing empirically derived substituent constants for the prediction of vicinal coupling constants in substituted ethanes. *Magn. Reson. Chem.* **1985**, *23*, 335–343.

(15) Meng, X.; Zhao, G.; Xu; Q.; Tan, Z.; Zhang, Z.; Jiang, L.; Shu, C.; Wang, C. -R.; Li, Y. Effects of Fullerene Bisadduct Regioisomers on Photovoltaic Performance. *Adv. Funct. Mater.* **2014**, *24*, 158-163.

(16) Zhou, F.; Meng, X.; Feng, Y.; Jin, Z.; Zhou, Q.; Li, H.; Jiang, L.; Wang, J.; Li, Y.; Wang, C. -R. Single crystalline indene-C_{60} bisadduct: isolation and application in polymer solar cells. *J. Mater. Chem.* A **2015**, *3*, 14991-14995.

(17) Shi, W.; Hou, X.; Liu, T.; Zhao, X.; Sieval, A. B.; Hummelen, J. C.; Dennis, T. J. S. Purification and electronic characterisation of 18 isomers of the OPV acceptor material bis-[60]PCBM. *Chem. Commun.* **2017**, *53*, 975–978.

(18) Liu, T.; Abrahams, I.; Dennis, T. J. S. Structural Identification of 19 Purified Isomers of the OPV Acceptor Material bisPCBM by ^{13}C NMR and UV−Vis Absorption

Spectroscopy and High-Performance Liquid Chromatography. *J. Phys. Chem. A* **2018**, *122*, 4138–4152.